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Infrared and infrared emission spectroscopy of the zinc carbonate mineral smithsonite

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Abstract

Infrared emission and infrared spectroscopy has been used to study a series of selected natural smithsonites from different origins. An intense broad infrared band at 1440 cm^{-1} is assigned to the ν_3 $CO_3{}^{2-}$ antisymmetric stretching vibration. An additional band is resolved at 1335 cm^{-1}. An intense sharp Raman band at 1092 cm^{-1} is assigned to the $CO_3{}^{2-}$ symmetric stretching vibration. Infrared emission spectra show a broad antisymmetric band at 1442 cm^{-1} shifting to lower wavenumbers with thermal treatment. A band observed at 870 cm^{-1} with a band of lesser intensity at 842 cm^{-1} shifts to higher wavenumbers upon thermal treatment and is observed at 865 cm^{-1} at 400 °C and is assigned to the $CO_3{}^{2-}$ ν_2 mode. No ν_2 bending modes are observed in the Raman spectra for smithsonite. The band at 746 cm^{-1} shifts to 743 cm^{-1} at 400 °C and is attributed to the $CO_3{}^{2-}$ ν_4 in phase bending modes. Two infrared bands at 744 and around 729 cm^{-1} are assigned to the ν_4 in phase bending mode. Multiple bands may be attributed to the structural distortion ZnO_6 octahedron. This structural distortion is brought about by the substitution of Zn by some other cation. A number of bands at 2499, 2597, 2858, 2954 and 2991 cm^{-1} in both the IE and infrared spectra are attributed to combination bands.

Keywords: Aurichaclite; Hydrozincite; Smithsonite; Rosasite; Hydroxy carbonates; Infrared and Raman spectroscopy; Infrared emission spectroscopy

1. Introduction

Smithsonite is a secondary mineral of zinc formed in the oxidation zone of zinc bearing ore bodies hexagonal with point group 3 bar 2/m. The mineral is named for James Smithson, the founder of the Smithsonian Institution (USA). The mineral is renowned for its pearly lustre and comes in a range of colours which vary across all colours of the visible spectrum. Although it must be stated that no studies have been undertaken to explain the colours of smithsonite even though some chemical analyses of the coloured smithsonites have been undertaken. It is interesting that some chemical analyses of smithsonites from different origins was first published in 1898 by W.O. Crosby. Carbonates with intermediate sized divalent cations normally crystallise in the calcite structure [1]. Those with larger cations have an aragonite type structure.

Of the secondary minerals of zinc only two minerals are known namely smithsonite and hydrozincite. The formation of these minerals is controlled by the partial pressure of CO_2 [2,3]. According to the equation for the formation of hydrozincite $5ZnO\,(s) + 2CO_2\,(g) \leftrightarrow Zn_5(CO_3)_2(OH)_6\,(s)$ with $\log K = 10.32$ [2]. Thus ZnO is unstable with respect to hydrozincite at partial pressures above $10^{-5.16}$. If the partial pressure of CO_2 increases above $10^{-1.41}$ smithsonite formation is favoured according to the reaction $Zn_5(CO_3)_2(OH)_6\ (s) + 3CO_2\ (g) \leftrightarrow 5ZnCO_3\ (s) + 3H_2O\,(g)$. These results provide implications for the relative stability of hydrozincite and smithsonite. It is noted that hydrozincite may form from solutions resulting from the oxidized zone of a Pb–Zn ore body [2]. Thus zincite (ZnO) is a rare mineral and smithsonite is only stable at elevated CO_2 partial pressures. The partial pressure range for the stability of hydrozincite according to Williams is limited and no doubt this accounts for the scarcity of the mineral in nature [3]. The mineral can be readily synthesised in the laboratory and is often found in corrosion products of zinc [4–6].

The free ion, $CO_3{}^{2-}$ with D_{3h} symmetry exhibits four normal vibrational modes; a symmetric stretching vibration (ν_2),

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Table 1
Table of the infrared spectra of selected smithsonites

Smithsonite (New Mexico, aqua green)			Cadmian smithsonite (S. Ireland, yellow)			Smithsonite (Namibia, light pink)			Smithsonite (Mexico, clear rose pink)			Smithsonite (Namibia, light green)			Smithsonite (Namibia, clear)		
Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area	Centre	FWHM	% Area
3330	251.7	3.45															
			2832	63.5	0.57												
2495	69.6	1.65	2494	49.3	1.27	2493	63.2	1.12	2508	158.3	3.22	2506	110.0	2.40	2497	75.3	1.54
2363	17.0	0.11															
2336	64.6	0.50															
									2176	84.8	1.18						
						1822	13.5	0.08									
1813	31.0	0.33	1812	24.6	0.45	1807	19.0	0.26				1813	27.2	0.25	1813	31.2	0.36
															1509	53.3	2.01
1485	100.9	10.41	1487	96.3	13.59	1486	88.3	12.23	1483	95.6	16.44	1491	94.2	13.01			
															1440	127.6	15.12
															1436	129.9	26.35
1412	71.9	10.61	1416	82.3	17.40	1420	85.3	25.62	1418	85.2	27.37	1418	93.5	23.59	1418	37.5	2.08
1389	164.4	33.47	1376	160.0	27.66												
						1357	173.7	24.65	1359	138.8	17.08	1358	154.6	25.34			
															1335	182.5	23.10
									1240	227.9	21.93	1222	207.9	19.79			
						1195	315.5	25.98									
															1152	264.6	20.01
1231	249.1	26.44	1236	241.8	26.58												
									1086	25.5	0.14						
1045	112.8	2.56	1037	173.1	2.51				1051	159.7	2.15	1046	160.4	2.43			
961	73.0	1.01							946	47.4	0.90						
872	12.4	1.02	874	10.3	0.75	873	12.0	1.72	874	10.4	0.92	873	14.4	1.32	874	11.4	1.27
863	18.0	2.08	867	13.7	1.77	864	13.4	1.95	867	13.5	2.11	864	19.1	2.02	867	13.9	1.91
844	32.6	2.14	857	19.0	1.57	853	15.0	0.96	856	18.7	1.60	846	32.9	1.83	855	16.7	0.98
840	3.2	0.02	840	5.4	0.11	840	10.5	0.22	840	10.7	0.31	840	4.3	0.03	840	6.0	0.14
			838	30.8	1.55	834	34.0	1.33	832	37.2	1.37				839	33.8	1.35
811	56.6	1.64	807	39.2	1.13	799	48.1	1.06	795	42.2	0.75	812	51.5	1.22	802	49.6	1.10
			778	21.8	0.21												
744	7.3	0.62	743	7.0	0.64	744	6.5	0.74	744	6.8	0.68	744	7.2	0.66	744	6.5	0.71
738	10.9	0.48	738	11.1	0.58	739	8.8	0.52	739	9.9	0.53	738	8.1	0.30	739	9.8	0.54
729	18.8	0.50	727	20.1	0.67	732	14.0	0.48	731	16.0	0.50	729	14.9	0.58	730	16.3	0.49
712	34.6	0.58	707	25.6	0.61	719	25.3	0.64	717	25.7	0.48	712	33.3	0.55	714	32.6	0.59
						693	32.9	0.45	690	48.6	0.33						
676	70.2	0.38	683	67.9	0.38							677	13.5	0.22	684	64.0	0.34
												525	0.0	4.47			